

## THE ROLE OF THE CF<sub>2</sub> RADICAL IN EXTINGUISHMENT

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### INTRODUCTION

Among the reactions that can be written for the CF<sub>2</sub> radical are the following.



Taken as a group, these three reactions suggest that the CF<sub>2</sub> radical might be involved in one or more catalytic cycles that remove flame propagating radicals from the flame. Reaction (1) is, of course, the primary elementary reaction by which HCF<sub>2</sub> is introduced into the chemistry of the flame, and occurs readily in typical flames. By contrast with HCF<sub>2</sub>, CF<sub>3</sub> is relatively unreactive in flames; the abstraction of an F atom does not occur easily. This then suggests that a comparison of the extinguishment effectiveness of HCF<sub>2</sub> with the extinguishment effectiveness of CF<sub>3</sub> should yield useful information as to the potential role of the CF<sub>2</sub> radical. If the differences in effectiveness are significant and cannot be explained in terms of small differences in heat capacities, then it would be reasonable to conclude that the CF<sub>2</sub> radical does make a significant contribution as a "chemical catalytic" extinguishing agent.

### EXPERIMENTAL

The experiments suggested here have been done in our laboratories. In these experiments, the heat removed from the flame is used as measure of the degree of extinguishment, with extinguishment being the point at which no heat is removed by the burner.

The Sapphire 0-4 Burner used in these experiments is a modified laboratory Meker burner (diameter = 3.7 cm). The heat absorbed by the burner is carried off by ethylene glycol, circulated at a measured flow rate by a gear pump through a cooling loop (3/16" copper tubing) silver soldered to the outside of the burner rim. The increase in the temperature of the ethylene glycol is measured by a pair of

thermocouples, located in the cooling loop just below the points of attachment of the loop to the burner rim.

In these experiments, the agent was premixed with methane and "air" (21% O<sub>2</sub>, 89% N<sub>2</sub>). The flow rates of agent and "air" were fixed, and the flow rate of CH<sub>4</sub> was "scanned" from the lean extinguishment limit to the rich extinguishment limit. At each value of the fuel-air equivalence ratio,  $\phi$ , the inhibited flame was compared with an identical (except for the absence of the agent) uninhibited flame.

## RESULTS

Figure 1 compares the uninhibited flame with flames inhibited by the same amounts of CF<sub>3</sub> and HCF<sub>3</sub>. It is immediately noted that HCF<sub>3</sub> removes very little heat from lean flames, while CF<sub>3</sub> extinguishes these flames; conversely, fuel-rich flames are extinguished by HCF<sub>3</sub> but not by CF<sub>3</sub>.

Figure 2 plots these data in a different fashion, and illustrates the regions in which each agent is the more effective. In this figure, the energy absorbed by the burner from an uninhibited flame is once again displayed. Superimposed for each agent is a data set which shows the magnitude by which the agent reduces the amount of heat absorbed by the burner. This reduction in the amount of heat absorbed by the burner is a combination of two factors: cooling due to the heat capacity of the agent, and inhibition of the flame chemistry due to the fact that fewer molecules (in the cooler flame) have adequate energy to surmount the activation energy barrier. It can be shown by a straightforward heat balance that the second of these two factors is by far the larger. It is evident from Figure 2 that CF<sub>3</sub> is nearly equally effective at all values of  $\phi$ , while HCF<sub>3</sub> has very little effect on lean flames, but has a larger effect than CF<sub>3</sub> on rich flames.

It is proposed that these differences can be explained simply in terms of the "fuel content" of HCF<sub>3</sub> as illustrated by the following overall stoichiometry.

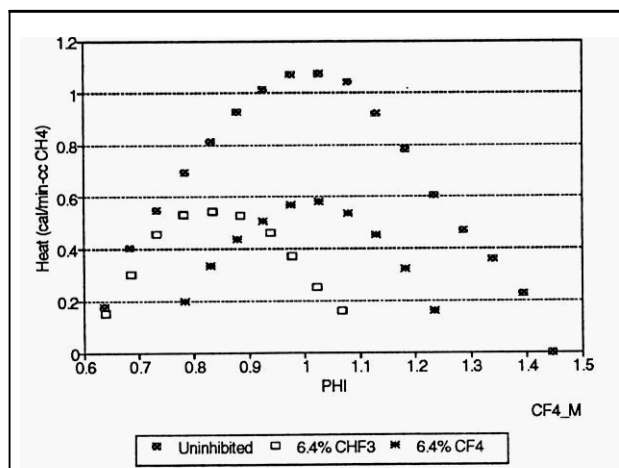
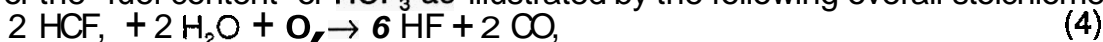


Figure 1. Heat Removed by burner

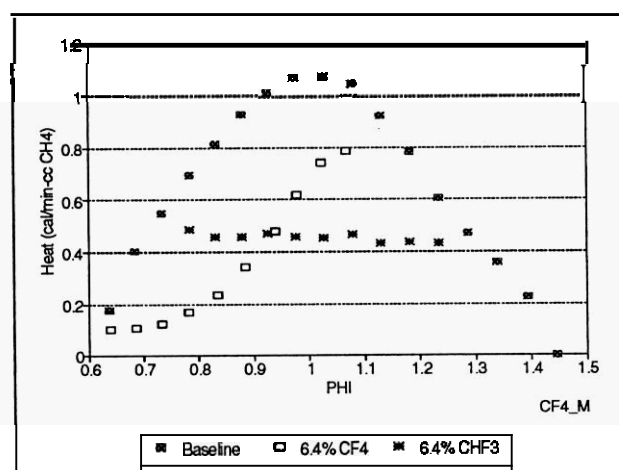


Figure 2. Reduction in Heat Absorbed by Burner

This equation suggests that some of the oxygen is used in combustion of the HCF, and that the fuel-air equivalence ratio,  $\phi$ , for combustion of CH, should be altered to reflect the availability of less oxygen. When this is done, Figure 3 is obtained. In this figure, the heat absorbed by the burner as a function of  $\phi$  is seen to be nearly identical for both agents. This finding is consistent with a model in which the dominant mechanisms of the two agents are both the same (physical); HCF, does alter the chemistry of the flame (but only to the degree that it serves as a fuel). The heat capacities of these two agents differ by less than 5% at typical flame temperatures, with CF<sub>4</sub> having the greater heat capacity.

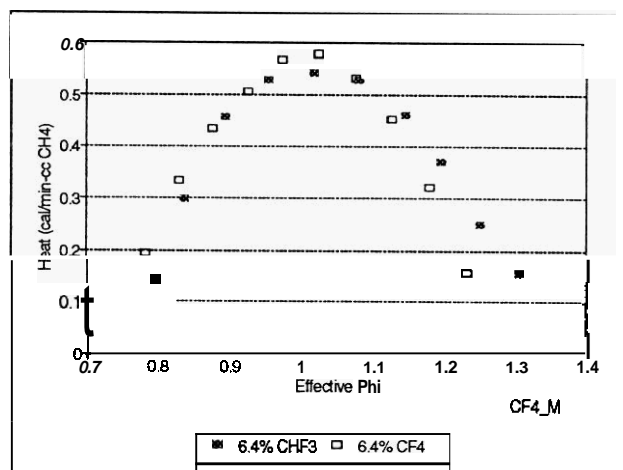
## CONCLUSION

There is no persuasive evidence for the hypothesis that the CF<sub>3</sub> radical might be serving as a "catalytic chemical" agent. Needless to say, this "back-of-the-envelope" argument needs to be substantiated by careful modeling. Moreover, it would be of value to test this conclusion on another pair of compounds such as C<sub>2</sub>F<sub>6</sub> and C<sub>2</sub>HF<sub>5</sub>.

## ACKNOWLEDGEMENTS

The principal authors gratefully acknowledge the work of the two undergraduate students who contributed to this work. Justin Schiro was the 1995 NSF REU student who suggested and conducted the first experiments in our laboratories in which  $\phi$  is scanned for a fixed amount of added extinguishing agent. Chris Spencer is still working with us and made all the careful measurements reported here.

This work was supported by the Air Force Office of Scientific Research, Contract No. F49620-94-1-0241.



**Figure 3.** Heat Removed by Burner;  $\phi$  Adjusted for Consumption of O<sub>2</sub> by HCF<sub>3</sub>

